
Use of STOs in Hartree–Fock Calculations: Error Analysis and Variance-Minimized Pseudospectral Method

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ABSTRACT: In this study it is demonstrated that STO (Slater-type orbital) basis sets are particularly well suited to pseudospectral Hartree–Fock calculations. The reduction of two-electron integrals, to ones that are (at worst) equivalent to a one-electron integral over three centers, eliminates the need for slowly convergent one-center expansions. This allows all integrals to be calculated quickly and accurately in either spherical or ellipsoidal coordinates. A new variance-minimized variant of the pseudospectral method is derived and applied to a number of small closed-shell molecules. The performance of the algorithm is assessed relative to purely spectral calculations employing STO and GTO (Gaussian-type orbital) basis sets. The pseudospectral operator is used to assess the errors contained in solutions found by the purely spectral method. The suitability of a number of different de-aliasing set types is also examined. Orthogonal sets of hydrogen-like eigenfunctions were found to be optimal.
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Introduction

Many years ago, Roothaan and Hall^{1,2} demonstrated that an optimal many-electron wave function, with the required property of antisymmetry with respect to an exchange of any two electrons, can be obtained using the usual linear-variation method, if an appropriate operator is applied iteratively to a set of atomic orbitals. For closed-shell systems they described how to construct such an operator and how to impose the orthonormality constraint using:

$$\det(\mathbf{F} - \lambda \mathbf{S}) = 0 \quad (1)$$

and

$$\mathbf{F}\mathbf{c}_i = \lambda_i \mathbf{S}\mathbf{c}_i \quad (2)$$

effectively minimizing the quantity:

$$\langle \mathbf{E} \rangle = \frac{\Phi^* \mathbf{F} \Phi}{\Phi^* \mathbf{S} \Phi} \quad (3)$$

where \mathbf{F} is the linear Hartree–Fock operator with one- and two-electron components and Φ is the many-electron wave function expressed as a Slater determinant with n electrons in n spin orbitals. The spin orbitals (χ) are formed from the product of a space part (ψ) and a spin part (ω). The space part of each spin orbital is expressed as a linear combination of atomic orbitals (φ). The linear coefficients are contained in the column vector, \mathbf{c} .

The reformulation of the essentially nonlinear Hartree–Fock equations into a linear one, in addition to simplifying the solution process, allows a wide range of analytical and numerical techniques to be employed that would otherwise be unsuitable. Many possibilities have been explored—finite-difference and various finite-element techniques,^{3–8} variance-minimization methods,^{9–17} and, more recently, the pseudospectral method.^{18–23}

The most difficult integral to evaluate in conventional (or purely spectral) Hartree–Fock (HF) and configuration–interaction (CI) calculations is the two-electron integral over four centers; in traditional density-functional (DF) calculations it is the two-electron integral over three centers. The conventional qualifier is used here to refer to those calculations in which the variational principle is used to find the linear combination of atomic orbitals (LCAO) that minimizes the expected value

of electronic energy. Due to the poor quality of even the best LCAO wave functions (this will be illustrated) the product of the Hamiltonian operator and the wave function is usually poorly represented in the argument space, with the error being referred to as the alias. The alias is not, however, an insurmountable problem if solutions are found using the variational method.

The most difficult integral in pseudospectral HF, CI, and DF, calculations is equivalent to a one-electron integral over three centers. In pseudospectral calculations, the Hamiltonian operator is applied to a vector in a continuous (or spectral) space, producing a vector in a discrete Cartesian space. In the pseudospectral approach of Friesner,¹⁸ a set of continuous interpolating functions (dealiasing functions) is then least-squares fitted to the discrete representation of $\mathbf{H}\Psi$, bringing the product back into a spectral space. The integration of $\Psi^* \mathbf{H} \Psi$, required by the variational method, is then accomplished using a rectangular matrix of overlap-type integrals. The use of a numerical integration scheme, applied to all basis functions collectively in a single step, greatly reduces the computational effort and storage required to integrate over the coordinates of the “second” electron. The discrete variable representation (DVR) method of Light, commonly used to solve molecular vibration problems, is similar, but the final integration is evaluated using Gaussian quadrature.^{24,25} It will be shown that variational methods are not necessary when a pseudospectral operator is used. The representation of $\mathbf{H}\Psi$ in a discrete space means that the (general) eigenvalue problem can be solved directly, in a least-squares sense, thus eliminating the need for the final integration.

Reexpressing the Roothaan–Hall equations in terms of one-center integrals represents a substantial reduction in the cost of molecular Hartree–Fock calculations. Complete working versions using GTO (Gaussian-type orbital) basis sets are now in circulation²⁶ and awareness of the method is growing. Pseudospectral calculations are being used to investigate transition-metal complexes²⁷ and in correlated electron (Moller–Plesset, configuration interaction and local space) calculations.^{28–30} The efficiency of the algorithm has recently been demonstrated with the treatment of relatively large systems using relatively modest computing power and large basis sets.^{31,32} Further enhancements can be expected with the refinement of parallel implementations of the algorithm.^{33,34}

STOs are particularly well suited to pseudospectral calculations, or to any calculation in

which the electronic potential is approximated on a discrete grid, because only a single diffuse charge distribution appears in the two-electron integrands. Integrals involving the $1/r_{12}$ operator and more than one diffuse charge distribution, expressed as the product of two STOs on different centers, are extremely difficult to evaluate.³⁵ Ellipsoidal coordinate expansions cannot be used for these integrals so other less efficient methods must be applied. This means that pseudospectral methods eliminate the types of integrals that have, to date, prevented STO basis sets from being used in medium to large molecules.

The advantages to be gained from expressing many-electron wave functions in the form of STOs are manifold. The fact that a small STO basis sets can do the work of a large GTO basis set is widely appreciated. The commonly overlooked benefit, however, is the ease with which STO basis sets can be constructed to suit a particular problem. Using effective-charge considerations, exponential arguments can be adjusted intuitively, thus eliminating the need for least-squares fitting procedures or pretabulated basis-set libraries. But, interest in STO basis sets has waned as the difficulties associated with evaluating two-electron integrals over three and four centers became apparent and as knowledge of the relatively simple procedures for evaluating many-center GTO integrals became more widespread.^{36–40} Despite recent attention,^{41–45} the computational difficulties associated with the evaluation of the more difficult STO integrals persists. The evaluation of one-electron integrals over three centers is, however, a comparatively simple process. Although many methods have been studied—one-center zeta-function expansions,^{41,46–49} Fourier transforms using a B-function basis,^{50,51} and expansions for $1/r_{12}$ in ellipsoidal coordinates^{41,52,53}—the speed and accuracy of the ellipsoidal-coordinate method makes it by far the most attractive alternative.

In this communication, it is recommended that the best—or perhaps the only—way to use STOs in Hartree–Fock calculations is to use the pseudospectral operator. It is further suggested that the eigenfunctions of the pseudospectral operator be found directly by minimizing the variance of the local energy instead of using the more usual variational (mean-minimized) approach. The use of the local energy function in the variance-minimized method leads naturally to a means by which the merit of a given solution, found by any method, can be assessed using the deviation of the local energy function about its mean.

Pseudospectral Hartree–Fock Operator

The pseudospectral Hartree–Fock operator (**F**) is a rectangular n_{points} by n_{basis} matrix. It acts on a vector of n_{basis} continuous basis functions, **c**, producing a vector (**F**), evaluated at the set of n_{points} discrete points in Cartesian space. The elements of **F** are found using:

$$F_{p,i} = H_{p,i} + G_{p,i} \quad (4)$$

where **H** and **G** are the one- and two-electron components of the Hartree–Fock operator, respectively. The one-electron component is the sum of kinetic (**T**) and nuclear potential terms (**V**):

$$H_{p,i} = T_{p,i} + V_{p,i} \quad (5)$$

$$T_{p,i} = -\frac{1}{2}\nabla^2\varphi_i(x_p, y_p, z_p) \quad (6)$$

and

$$V_{p,i} = -\sum_k q_k \frac{1}{r_{12}} \varphi_i(x_p, y_p, z_p) \quad (7)$$

where q_k is the charge of the k th nuclei, located at (x_k, y_k, z_k) , and r_{12} is the distance between (x_k, y_k, z_k) and the p th sample point at (x_p, y_p, z_p) . For a closed-shell system the two-electron component is the simply the sum of Coulomb (**J**) and exchange terms (**K**):

$$G_{p,i} = J_{p,i} - \frac{1}{2}K_{p,i} \quad (8)$$

$$J_{p,i} = \sum_{k'} \sum_k c_{k'} c_k \int \varphi_{k'}(x_2, y_2, z_2) \times \varphi_k(x_2, y_2, z_2) \frac{1}{r_{12}} \varphi_i(x_p, y_p, z_p) dv_2 \quad (9)$$

and

$$K_{p,i} = \sum_{k'} \sum_k c_{k'} c_k \int \varphi_{k'}(x_2, y_2, z_2) \times \varphi_i(x_2, y_2, z_2) \frac{1}{r_{12}} \varphi_k(x_p, y_p, z_p) dv_2 \quad (10)$$

where r_{12} is the distance between the p th sample point and the volume element dv_2 .

If an orthonormal basis set is used then the eigenvalues of the following equation are the one-electron energies of the optimal molecular orbitals (MOs):

$$\mathbf{A} = \mathbf{WR}^{-1}\mathbf{F}. \quad (11)$$

\mathbf{R}^{-1} is the pseudo-inverse of \mathbf{R} . If there are $n_{de-alias}$ de-aliasing functions (ϕ), then \mathbf{R} is a rectangular n_{points} by $n_{de-alias}$ matrix. Element $R_{p,j}$ is the j th de-aliasing function evaluated at the p th point in space:

$$R_{p,j} = \phi_j(x_p, y_p, z_p) \quad (12)$$

The singular-value decomposition of \mathbf{R} is an efficient means of obtaining \mathbf{R}^{-1} ; that is, if $\mathbf{R} = \mathbf{USV}^{-1}$, then $\mathbf{R}^{-1} = \mathbf{VS}^{-1}\mathbf{U}^{-1}$.

\mathbf{W} a rectangular n_{basis} by $n_{de-alias}$ matrix with the overlap between the i th basis function and the j th de-aliasing function as elements:

$$W_{i,j} = \int \varphi_i(x_1, y_1, z_1) \phi_j(x_1, y_1, z_1) dv_1 \quad (13)$$

The elements of the square matrix, \mathbf{A} , in eq. (11), are physically equivalent to the elements of the Hartree–Fock matrix in the Roothaan–Hall method. Friesner’s pseudospectral method and the purely spectral method of Roothaan and Hall are both mean-minimized methods. They find wave functions that minimize the expected value of energy according to the variational principle. The manner in which the pseudospectral method accomplishes this is perhaps clarified by describing how each of the product terms comprising \mathbf{A} interact with each other:

- \mathbf{F} operates on a vector (\mathbf{c}), of length n_{basis} , in continuous space producing a vector (\mathbf{f}), of length n_{points} , in discrete space.
- \mathbf{R}^{-1} fits the de-aliasing functions to \mathbf{f} , in a least-squares sense, producing a vector (\mathbf{a}), of length $n_{de-alias}$, in continuous space.
- \mathbf{W} integrates the product of the de-aliasing vector (\mathbf{a}) and the transpose of the basis function vector (\mathbf{c}^t).

The orthonormality constraint, imposed upon the linear variational procedure [eq. (11)], can be enforced by the construction of an orthonormal basis set from the set of overlapping basis functions. This is done in the usual way by transforming \mathbf{A} using $\mathbf{X}^t\mathbf{A}\mathbf{X}$, where \mathbf{X} is an n_{basis} by n_{basis} matrix with a set of vectors that transforms the overlap matrix (\mathbf{S}) into the identity matrix (\mathbf{E}) as its columns. \mathbf{X}^t is the inverse of \mathbf{X} (\mathbf{X} is an orthogonal matrix because \mathbf{S} is symmetric).

After the selection (or construction) of an appropriate basis set, a number of important measures must be taken to ensure that the pseudospectral molecular orbitals are equivalent to those found using the purely spectral method. First, the de-aliasing set should be capable of faithfully representing the result of the application of \mathbf{F} on any given trial vector \mathbf{c} . With too few de-aliasing functions, important features of the operation may be omitted. Too many may cause problems during the singular-value decomposition of \mathbf{R} . Tazartes et al. applied an algorithm used in the field of statistical signal processing to optimally fit Gaussian de-aliasing functions to the discretely sampled quantity represented by \mathbf{f} .⁵⁴ In this investigation, four different types of de-aliasing sets are used. The first set is identical to the basis set. The second set is composed of a large number of functions, resembling the basis set, but with a wider range of exponential arguments and powers of r . This is the type of de-aliasing set used by Friesner and coworkers,^{18–23} although they used GTOs instead of STOs. The third set is the same as the second, but augmented by a number of potential-type functions of the form $1/r$ and $\exp(-r)/r$. These were used because the residual features of the electrostatic potential appearing in the two-electron component of the Hartree–Fock operator are likely to appear in \mathbf{f} . The fourth set tested is built from a number of hydrogen-like eigenfunctions. In this case, all de-aliasing functions on a given center form an orthonormal subset; therefore, from the theory of orthogonal functions one might expect a more accurate representation of \mathbf{f} when small de-aliasing sets are used and a reduced likelihood of numerical problems when large sets are used. The location and number of the sample points is of course another important concern. Ringnalda et al. suggested the use of grids derived from Gaussian-quadrature schemes.²³ The fusion of local atomic grids into a global molecular grid and the calculation of the corresponding weights is not a trivial matter. Fortunately, there are many molecular integration strategies in the literature that might be used as a guide.^{55,56} The use of de-aliasing functions, however, eliminates the need for perfectly constructed molecular grids and weights because the integrand is expressed as the sum of de-aliasing-function and basis-function products, which can be evaluated using the analytical overlap-type integrals appearing in the \mathbf{W} matrix.

Local Energy Function and Variance-Minimized Pseudospectral Calculations

Ideally, the objective of an electronic calculation is to obtain a wave function with a constant local energy over all space and spin coordinates. In nearly all cases, however, an approximate wave function must suffice. Approximate solutions found using the variational principle yield a wave function for which the weighted deviation of the local energy function away from its weighted mean is minimized. The most appropriate weight function is, of course, the probability density. The total energy is minimized with respect to the adjustable parameters and so is the variance of the local energy. Whereas the analytical evaluation of the expected value of energy of a wave function is relatively simple, the difficulties associated with the accurate representation, and integration, of the local energy function usually rules out its explicit use in the calculation process. These difficulties are, however, bypassed when the local energy is sampled over a finite set of points. The local energy statistics in this space can be used either as a means of solving the molecular Schrödinger equation or as a means of assessing the accuracy of a wave function found by another method. As an error probe, the local energy might be sampled only in specific regions of physical significance and used to assist in the selection of a basis set or method. Although error estimates are considered essential in engineering software, they have not as yet been incorporated into first-principles chemistry packages, which are being used increasingly in a design role.

Dividing the Schrödinger equation, $E\Psi = \mathbf{H}\Psi$ by Ψ yields:

$$E_{loc} = \frac{\mathbf{H}\Psi}{\Psi}. \quad (14)$$

E_{loc} is equal to a constant for an exact solution. For an approximate (normalized) solution, the multiplication of both sides by the probability density

$\Phi^*\Psi$, and integrating, yields the more familiar mean of the local energy:

$$\langle E \rangle = \int \Psi^* \mathbf{H} \Psi. \quad (15)$$

The local energy function was first used by Bartlett^{9,10} to analyze and improve the correlated helium wave function. Frost^{11,12} pointed out that any method that can be used to *assess* errors in solutions can also be used to *find* solutions. He then set about devising a method based on the minimization of the local energy variance with respect to a set of linear parameters, where:

$$\sigma^2 = \int \Psi^* \Psi (E_{loc} - \langle E \rangle)^2. \quad (16)$$

Using a predefined set of basis functions, Frost expressed the linear least-squares problem in matrix form and found an approximate solution to the ionized hydrogen molecule using an iterative process. A similar method, using weight functions other than the probability density, has been recently applied to the same system by Feldkamp.⁵⁷ For many-electron Hamiltonians, the squaring of the difference in eq. (16) produces rather convoluted product terms that are prohibitively difficult to integrate, making the method unsuitable for general many-electron calculations. For this reason, the method has not been used in molecular calculations.

King and Dalke devised a less severe approach in which the Hartree-Fock equations are solved by finding the wave function that minimizes the expected value of energy, in addition to satisfying a set of local energy constraints.¹³ The auxiliary conditions state that the difference between the local Hartree-Fock energy and the mean Hartree-Fock energy must be below a specified threshold at a set of arbitrarily selected points in space. Unfortunately, the extra constraints necessitate the use of complicated nonlinear techniques to solve the problem. In their calculations, King and Dalke used a more general form of the local energy, one that incorporates the space and spin coordinates of many-electron wave functions in a more natural manner. They used:

$$E_{loc}(1) = \frac{\int \Psi^*(1,2,\dots,n) \mathbf{H} \Psi(1,2,\dots,n) ds_1 ds_2 \dots ds_n dr_2 \dots dr_n}{\int \Psi^*(1,2,\dots,n) \Psi(1,2,\dots,n) ds_1 ds_2 \dots ds_n dr_2 \dots dr_n} \quad (17)$$

where $E_{loc}(1)$ is the "one-electron reduced local energy function." This expression, originally defined by Thomas et al.,¹⁴ appeals to the notation and concepts used by Lowdin.⁵⁸ The space coordinate of the first electron is the only coordinate not involved in the integration; therefore, $E_{loc}(2)$ is a function of x_1 , y_1 , and z_1 only. As Ψ is antisymmetric, E_{loc} is the same, regardless of which electron is selected. If Ψ is a Slater determinant (Φ), with doubly occupied MOs (ψ), then eq. (17) is the same as the sum the local energy function of each MO, multiplied by a normalizing factor of $2/n$. The local energy function, as defined in eq. (17) for many-electron systems, has been used to optimize STO basis sets for the first-row transition metals.¹⁵ It has also been used to investigate errors contained in correlated wave functions,¹⁴ and approximate wave functions for the helium isoelectric series¹⁶ and a variety of small molecules¹⁷ calculated using GTO basis sets.

A new method for the calculation of approximate many-electron wave functions, using the local energy function and STO basis sets, will now be outlined and applied to the ten-electron series (neon, hydrogen fluoride, water, ammonia, methane, and diatomic boron). The method is essentially a variant of Friesner's pseudospectral approach. It involves the same pseudospectral operator, but it uses the minimization of the local energy variance as its solution criterion (variance minimized) instead of the minimization of the expected value of total energy (mean minimized).

The concept of local energy is lost in most LCAO approaches because of the difficulties associated with the analytical representation of the quantity. This is not the case, however, when the pseudospectral Hartree-Fock operator is used, because a points-in-space-type basis is much more flexible. The ability of such a basis to resolve any spatially continuous function, of course, increases with the density of points. As mentioned previously, the pseudospectral operator is a rectangular matrix that operates in a spectral space (on a set of continuous basis functions, \mathbf{c}) producing a vector in Cartesian space (a set of discrete points, \mathbf{f}). For an exact solution, the result of the operation is a scalar multiple of the discrete representation of the original continuous vector:

$$\lambda \mathbf{Yc} = \mathbf{Fc} \quad (18)$$

where $\mathbf{f} = \mathbf{Fc}$ and $\mathbf{y} = \mathbf{Yc}$.

\mathbf{Y} is a rectangular n_{points} by n_{basis} matrix. The element $Y_{p,i}$ is the evaluation of the i th basis

function at the p th point. As before, \mathbf{F} is the n_{points} by n_{basis} pseudospectral Hartree-Fock operator, $\mathbf{F} = \mathbf{H} + \mathbf{G}$. If the function, $f_i(x, y, z)$ represented by the vector \mathbf{f} , is the result of the operation of the Hartree-Fock operator on the i th basis function, then the element $F_{p,i}$ is the evaluation of f_i at the p th point (x_p, y_p, z_p). The scalar, λ , is the energy corresponding to the one-electron solution, \mathbf{c} .

Eq. (18) is a general eigenvalue problem. Exact solutions only exist when \mathbf{F} and \mathbf{Y} are square; that is, when the number of points is equal to the number of basis functions. In most cases, however, is required for sensible results. For rectangular matrices, the general eigenvalue problem is solved in a least-squares sense, automatically minimizing the deviation of the local energy from its mean. Eq. (18) can be reexpressed as a conventional non-symmetric eigenvalue problem by multiplying (from the left) by the pseudo-inverse of \mathbf{Y} , which is conveniently found via its singular-value decomposition.

It will be shown that eq. (18) yields satisfactory eigenfunctions and eigenvalues using only one-electron integrals; however, for an accurate expected value of electronic energy, an integration over the coordinates of a second electron must be executed after self-consistency has been reached. This can be done using:

$$\langle E \rangle = \frac{\mathbf{c}^t \mathbf{W} \mathbf{R}^{-1} \mathbf{F} \mathbf{c}}{\mathbf{c}^t \mathbf{S} \mathbf{c}} \quad (19)$$

here, $\mathbf{F} = 2\mathbf{H} + \mathbf{G}$ (for a closed-shell system).

The quality of the one-electron eigenfunctions can be assessed using plots of the discrete representation of E_{loc} , found by dividing every element in the vector \mathbf{f} by the corresponding element in \mathbf{y} . These quantities can be readily evaluated for a purely spectral calculation using the integrals evaluated on the grid of a pseudospectral-type calculation for that system. The expressions given in what follows can also be used to statistically characterize the merit of a solution:

$$\langle E \rangle_{sample} = \frac{(\mathbf{Rc})^t \mathbf{Fc}}{(\mathbf{Rc})^t \mathbf{Rc}} \quad (20)$$

and

$$\sigma_{sample}^2 = \frac{(\mathbf{Fc})^t \mathbf{Fc}}{(\mathbf{Rc})^t \mathbf{Rc}} - \langle E \rangle_{sample}^2 \quad (21)$$

It should be noted that interpolating functions are not used to evaluate these statistical parameters.

The mean given in eq. (20) should approach that of the eigenvalue as the density of sample points is increased.

Conversely, the analytical one- and two-electron integrals, used in a purely spectral calculation, can be used to calculate the expected value of electronic energy, thus providing a means of assessing the quality of the wave function and the accuracy of the integration over the coordinates of the second electron. The total energy calculated in this way will be referred to as the "analytical energy" as opposed to the total energy calculated directly using the mean- or variance-minimized pseudospectral method, which will be referred to as the "numerical energy." The pseudospectral results that follow were calculated exclusively using the variance-minimized variant of the pseudospectral method.

Computational Details

The total energies for the first-row ten-electron series, neon through to the diboron molecule, were calculated using three different types of GTO basis sets and Clementi's STO basis set.⁵⁹ Clementi's basis set has never been used extensively in molecular calculations. It is a double-zeta best-atomic basis set, containing two STOs for each atomic orbital (AO). The exponents of each orbital were found using a nonlinear algorithm that iteratively minimized the expected value of electronic energy, for the atomic systems lithium through to argon. Clementi did not define a basis set for the hydrogen atom. In this work, a single basis function was used, greatly reducing the number of many-center integrals. To compensate for the reduced flexibility of the single-zeta basis, its exponent (a) was systematically adjusted according to the degree of ionicity/covalency of the bond it forms ($a = 1.2$ in CH_4 , 1.3 in NH_3 , 1.4 in H_2) and 1.5 in HF). The basis sets and geometries used in all calculations were identical for a given system.

The GTO calculations were implemented using TURBOMOLE.⁶⁰ The standard double-zeta (dz) and triple-zeta (tz) basis sets were used. The popular 6-31g basis, from the GAUSSIAN package,⁶¹ with a single-zeta subset for the core region and a double-zeta subset for the valence region, was also employed. In these basis sets, each "contracted" basis function is a linear combination of primitive Gaussian functions. The linear coefficients have been optimized to produce good results for a wide

range of trial molecules. The contraction process decreases the dimensionality of the Hartree-Fock problem and greatly reduces the number of integrals requiring storage. At least six primitives are usually required to emulate the exponential decay of the core orbitals. In the valence region, where flexibility and long-range decay become relatively more important, it is better to have more basis functions, each with fewer Gaussian primitives.

Code for implementing the spectral and pseudospectral algorithms⁶² was written in FORTRAN90. Its in-built matrix and vector types and the availability of efficient numerical libraries made it the most suitable programming language. The integrals, evaluated by a suite of C++ procedures, were read from binary disk files. The algorithms implemented in these procedures have been described in detail elsewhere.⁴¹ All that needs to be mentioned here is that the purely spectral method uses one-center zeta-function expansions, which converge slowly and produce terms that require numerical evaluation, to evaluate all two-electron integrals over three and four centers, and that both methods use expansions for $1/r_{12}$ in spherical and ellipsoidal coordinates to evaluate integrals over one, two, and three centers. The numerical parameters controlling the zeta-function expansions were relaxed somewhat and, in some cases, the procedures modified with an emphasis on speed. The zeta-function expansions were of course not required in the pseudospectral calculations. An L_{max} parameter of 4 was found to be sufficient for the ellipsoidal-coordinate routines. Due to the unpredictable occurrence of very small or zero integrals in the zeta-function procedure, and the consequent premature satisfaction of the convergence condition, all zeta-function expansions were terminated unconditionally at $T = 6$, which was more than sufficient for the systems examined here. The central "heavy" atom was used as the expansion center for all integrals involving STOs not centered on a hydrogen nucleus.

Clementi's best-atomic double-zeta STOs were used as basis sets in all pseudospectral calculations. The results obtained using these basis sets in purely spectral calculations were analyzed using statistical methods and compared. Four different types of de-aliasing sets were examined:

- The first type, "basis set only," is the same as the basis set used to build the solution.
- The second type, "large STO," is composed of a more extensive set of STOs. For each

basis function, the exponential argument (a) is set to double, equal, and half of the nuclear charge of the atom on which it is centered. A single STO with $a = 1$ is placed on each hydrogen nucleus.

- The third type, “augmented STO,” is the same as the “large STO” set, but it is augmented by Coulombic potential functions (STOs with a single negative power of r). One is placed on each center with a set equal to the nuclear charge of the atom on which it is centered.
- The fourth type, “hydrogen-like,” is composed of an orthogonal set of hydrogen-like eigenfunctions centered on each nucleus. The generating charge (Z) is set equal to the nuclear charge. Each set is truncated at $N = 4$ for the first row elements, and $N = 2$ for hydrogen, where N is the “principal” quantum number.

A number of grids with different radial and angular densities were tested. It is well known that partitioning the surface of a sphere by equally spaced “meridians” and “parallels” creates an uneven distribution of angular points, with a greater density at the “poles” than at the “equator.” This problem has been avoided in the past using a variety of different optimal distributions; however, it was utilized by the algorithm employed in this work. Around each atomic center, the θ coordinate was divided (from 0 to π) by $n_{par} + 1$ to create a “pole” and n_{par} “parallels.” The ϕ coordinate was divided (from 0 to 2π) by $n_{mer}/2$ to create n_{mer} “meridians.” The distribution of the radial points along the “rays” passing through each of the angular points increased in density exponentially near the nuclei.

With the angular and radial grid coordinates defined relative to the location of the atomic cen-

ter, the grid is then expressed in a Cartesian coordinate system originating at the atomic center. The grid thus generated is then rotated toward a center so that the poles of the atomic grids are aligned along the bond axis. The local atomic Cartesian system is then transformed into the single molecular Cartesian system. The total number of points used in all systems is listed in Table I. This method of grid generation is crude but simple. More rigorous methods, such as those outlined in refs. 55 and 56, will be investigated in future work.

Results and Discussion

Using the contents of Table II and variational principle as a guide, it is clear that the double-zeta STO wave functions are consistently better than the double-zeta GTO wave functions and consistently worse than the triple-zeta GTO, when employed in purely spectral calculations. For ammonia and methane, the total energy found using the 6-31g basis set is slightly lower than that found using the STO basis set. When execution speed is considered, however, the STO basis set is inferior to the GTO basis sets, even after speed differences due to the high degree of procedural optimization in the TURBOMOLE code is factored into the performance equation. The GTO calculations were all completed in less than a minute. The STO calculations were more than an order of magnitude slower. Even triple-zeta GTO basis sets, with “polarization” functions, and without contraction,

TABLE I.
Number of Pseudospectral Sample Points Used in Each System.

B ₂	CH ₄	NH ₃	H ₂ O	HF	Ne
196	392	336	280	224	168

TABLE II.
Total Molecular Energies (Hartrees) Calculated Using STO and GTO Basis Sets and the Purely Spectral Method.

System	Spectral dz	Spectral tz	Spectral 6-31g	Spectral STO	Pseudospectral STO (analytical)	Pseudospectral STO (hydrogen-like)
Ne	-128.467528	-128.540811	-128.473877	-128.534794	-128.348090	-127.701881
HF	-99.971090	-100.036940	-100.002756	-100.021271	-99.730651	-99.685022
H ₂ O	-75.969418	-76.021701	-75.985081	-75.999990	-75.667713	-75.679597
NH ₃	-56.147951	-56.185837	-56.163205	-56.162890	-55.881580	-55.528528
CH ₄	-40.169963	-40.189555	-40.180168	-40.170733	-40.063192	-40.073856
B ₂	-48.745187	-48.771339	-48.738858	-48.748650	-48.522029	-48.181399

TABLE III.
Approximate Wall-Clock Time (Minutes) for
Spectral and Pseudospectral Calculations Using
the STO Basis Set.

System	Spectral	Pseudospectral
Ne	0.02	0.1
HF	0.25	0.5
H ₂ O	9	1.2
NH ₃	97	2
CH ₄	337	2.8
B ₂	900	5.2

can be completed in around the same time it takes to do a double-zeta STO calculation. Any improvement in the wave function brought about by using double-zeta STO basis sets in spectral Hartree-Fock calculations, instead of double-zeta GTO basis-sets, is therefore meaningless. The same cannot be said of the pseudospectral algorithm, as the two-electron bottleneck is completely avoided. Table III shows that the lost execution time is recovered when the pseudospectral method is used. The replacement of the spectral method by the pseudospectral method does not bring about a speed enhancement for the neon and hydrogen fluoride systems, where a few two-electron integrals, over one and two centers, respectively, are replaced by many one-electron integrals over two and three centers.

The accuracy of the total Hartree-Fock energy, calculated using either of the pseudospectral methods, is critically dependent upon the type of de-aliasing set used. For variance-minimized pseudospectral calculations, the de-aliasing set affects only the total energy, not the form of the wave function. This is due to the fact that the eigenfunctions are found by evaluating the local energy function on the discrete grid. The variance-minimized pseudospectral method only uses the de-aliasing functions to integrate the product of the local energy and the probability density *after* the optimal self-consistent wave function has been found. The results of the variance-minimized pseudospectral method are presented in Table II. The necessary two-electron integrals were also evaluated so that the total energy of the wave function could be calculated exactly, for the sake of comparison. As previously mentioned, the total energies found in this way are said to be "analytical." The total energies found using the de-aliasing sets will be referred to as "numerical." Only the total energies found using the hydrogen-like

dealiasing set are shown. All pseudospectral calculations in Table II are variance minimized, with STO basis sets. The following points, all consequences of the variational principle, should be considered when assessing the tabulated results:

1. The lower the analytical energy, the better the wave function. It should be noted that the analytical energy is only available when all two-electron integrals have been calculated, in addition to the standard integrals required to execute the pseudospectral algorithm.
2. The closer the numerical energy is to the analytical energy, the more accurate the numerical integration scheme (i.e., the more appropriate the de-aliasing set).
3. For variance-minimized pseudospectral calculations, the type of de-aliasing set does not influence the analytical energy, assuming a high degree of self-consistency has been attained.
4. The total analytical energy of the pseudospectral wave function should not be lower than the optimal spectral wave function for calculations employing the same basis set.

The analytical pseudospectral energies are all slightly greater than the corresponding spectral energies, which suggests that the pseudospectral wave functions are not quite as good in the variational sense. The difference between the analytical and numerical energies suggests that there is room for further refinement of the integration grid and the de-aliasing set. The hydrogen-like de-aliasing set was superior to the other de-aliasing sets. There is only a small difference between the analytical and numerical energies when this set is employed. The other de-aliasing sets performed poorly and are not shown in Table II. The use of a de-aliasing set containing many "overlapping" STOs, with a wide range of exponential arguments and radial powers, does not necessarily guarantee an accurate Hartree-Fock energy. Friesner and coworkers reported agreement to six significant figures for spectral and pseudospectral calculations using GTO basis sets.²³

As it is implemented here, the variance-minimized pseudospectral method consistently gave better results than its mean-minimized counterpart. It converges more rapidly and to a greater degree of self-consistency. It is also slightly faster because the integration over the coordinate of the

second electron does not need to be evaluated at every SCF cycle, provided the total electronic energy is not used as the convergence criterion. Assuming self-consistency, the variance-minimized and mean-minimized pseudospectral methods, using the same molecular grid, de-aliasing set, and basis functions, produce nearly indistinguishable wave functions. This is noteworthy, as the two-electron integrals are numerically evaluated in the more usual mean-minimized method but they are omitted entirely in the variance-minimized method. In variance-minimized calculations, solutions are found without evaluating the total expected value of energy; therefore, the integral over the coordinate of the second electron need only be done if the expected value of energy is of particular interest. It is not necessary when the expected value of a different quantity is required, such as the dipole moment or electronic density. Due to convergence problems on these relatively sparse grids, the results of mean-minimized pseudospectral calculations are not shown.

To better illustrate the quantities being used in the variance-minimized pseudospectral method, the probability density and local energy function were sampled along a radial ray originating at the nucleus within the neon atom. The results are plotted in Figure 1 for the HF AOs produced by the purely spectral calculation using double- and quadruple-zeta basis sets. The plots of the f vector are interesting because they reveal what features the de-aliasing functions must have if they are to perform their least-squares fitting duty effectively.⁵⁴ The local energy plots reveal that the Hartree-Fock wave function is poor in the immediate vicinity of the nucleus. These plots also give an indication of how the local energy function varies over the AOs calculated by the purely spectral method. Clearly, the local energy is far from constant.

The improvement in the quality in the wave function bought about by the use of a more extensive basis set is much more apparent in the local energy function than it is in the total expected value of energy. Substituting a quadruple-zeta basis set for the double-zeta set in the neon atom yields a reduction in the total energy of less than 0.01%. Such an improvement may not appear to be worth the significantly greater computational effort, but the reward comes in the form of a two-orders-of-magnitude improvement in the local energy variance, demonstrating that the solution is

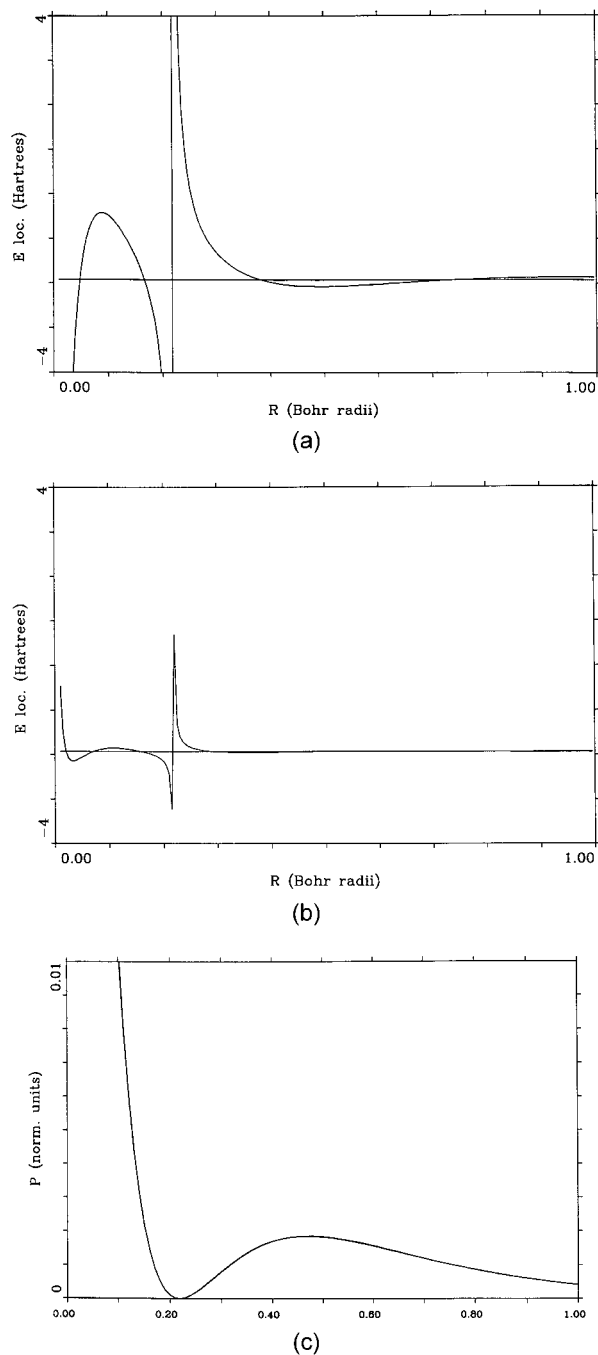


FIGURE 1. The local energy ($E_{loc.}$) of neon's 2s orbital, calculated using the purely spectral method and Clementi's best-atomic double-zeta basis set (a) and a quadruple-zeta basis set (b). The calculated probability densities for both basis sets (c). The probability densities are indistinguishable on this scale.

much closer to being an eigenfunction of the Hamiltonian operator. The results of both calculations are presented in Tables IV and V. The probability density and the local energy of the 2s orbital produced by both calculations are also compared in Figure 1. The probability densities are nearly identical, but the local energy functions are clearly dissimilar. The greater flexibility of the larger basis set allows the local energy discontinuity at the radial node and the divergence at the nuclei to be compressed more tightly into regions with a lower probability density, yielding a smaller weighted deviation away from the mean and a much "flatter" local energy profile. The probability density is greatest in regions of relatively constant local energy and approaches zero where the local energy approaches infinity. This effectively reduces the statistical weight of the solution in regions that contain large errors.

TABLE IV.
Statistical Analysis of Neon's Local Energy Spectrum, Calculated Using the Purely Spectral Method and Clementi's Best-Atomic Double-Zeta Basis Set.^a

Expected value (Hartrees)	Population mean (Hartrees)	Population variance (Hartrees ²)
- 32.760737	- 32.709830	0.007446
- 1.922401	- 1.099337	0.474936
- 0.842008	- 1.482192	2.330566
- 0.842008	- 1.482192	2.330566
- 0.842008	- 1.482192	2.330566

^aTotal atomic energy = -128.534794 Hartrees.

TABLE V.
Statistical Analysis of Neon's Local Spectrum, Calculated Using the Purely Spectral Method and a Quadruple-Zeta Basis Set.^a

Expected value (Hartrees)	Population mean (Hartrees)	Population variance (Hartrees ²)
- 32.772351	- 32.738245	0.000372
- 1.931250	- 1.889477	0.001699
- 0.850869	- 0.870585	0.037382
- 0.850869	- 0.870585	0.037382
- 0.850869	- 0.870585	0.037382

^aTotal atomic energy = -128.545465 Hartrees.

Conclusion

The computational effort required to evaluate two-electron integrals over STO basis functions on three or four centers makes it difficult for STOs to compete with GTOs as basis sets in purely spectral Hartree-Fock calculations. It has been shown that the pseudospectral method is able to benefit from the desirable functional form of STOs without incurring the computational penalty, because the most difficult integral requiring evaluation is equivalent to a one-electron integral over three centres. Fortunately, these integrals can be evaluated quickly and accurately within an ellipsoidal coordinate system. The much slower zeta-function expansions used to evaluate two-electron integrals over three and four centers are simply not necessary. Of the different de-aliasing sets investigated, hydrogen-like de-aliasing sets were found to be the most suitable. Large de-aliasing sets containing STOs, even with the addition of Coulombic functions, were unable to translate the result of the action of the pseudospectral Hartree-Fock operator on the wave function, from a discrete to a continuous space, to a sufficient degree of accuracy. The variance-minimized pseudospectral algorithm was derived and successfully applied to a set of sample molecules. The method is many times faster than the purely spectral algorithm and produces wave functions of a high quality. It was also shown that the pseudospectral operator can be used to assess the errors contained wave functions found via the purely spectral method. Knowing the regions in which the local energy deviates significantly away from the mean can be useful when considering the accuracy of expected values or the use of customized basis sets.

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